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Light-triggered covalent assembly of gold nanoparticles in aqueous solution†

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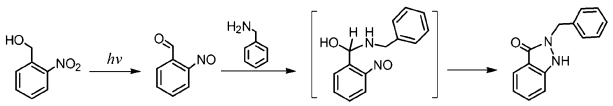
UV light irradiation triggers Au NPs that are respectively functionalized on the surface by *o*-nitrobenzyl alcohol and benzylamine to proceed with a covalent ligation reaction, which leads to assembling of Au NPs into anisotropic one-dimensional (1D) arrays in aqueous solution *via* indazolone linkages.

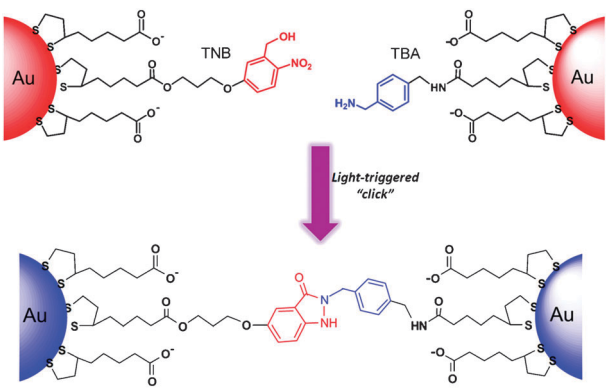
Assemblies of inorganic nanoparticles (NPs) in aqueous solution into one-, two- or three-dimensional architectures on the nanoscale have received considerable recent attention because of their potential applications in fields like electronics, photonics, catalysis and sensors.[1] Self-assembly provides a simple and low-cost means for producing ensembles of NPs in a controllable manner. A variety of approaches have been developed for assembling of NPs that are based on noncovalent interactions such as hydrogen bonding, electrostatic interaction and van der Waals interaction, specific biorecognition, chemical conjugation, polar interactions or employing polymer and biomacromolecules as binders.[1,2] Among them, approaches involving covalent interactions are attractive as they produce NPs assemblies of higher stability and not susceptible to disassembly under various solution conditions, *e.g.*, salt, pH and temperature.[3] However, only a few covalent reactions, *i.e.* gold–thiol bonding,[3a–d] amide chemistry,[3e,f] Diels–Alder reaction[3g] and click reaction[4,5] have been employed for covalent self-assembling of NPs. A challenge which remains in NPs assembling by most of the available approaches is that they usually lead to spherical or irregularly shaped aggregates, rather than specific architectures such as anisotropic chains, sheets, vesicles or three-dimensional (3D) crystals that are more valuable for the fabrication of optoelectronics and biosensor devices.[1] Therefore, approaches for covalently fabricating NPs in aqueous solution into anisotropic architectures are of particular interest and highly demanded.

In a previous study, we have shown that *o*-nitrobenzyl alcohol and benzylamine in aqueous solution can undergo an aldehyde–amine ligation-like coupling reaction under UV irradiation (Scheme 1).[6] The photolysis of *o*-nitrobenzyl alcohol rapidly generates *o*-nitrosobenzaldehyde in a quantum yield of 0.45, which subsequently condenses with benzylamine to lead to a thermally stable 2-(*N*-benzyl)indazolone with a reaction rate constant of 370 M^{-1} s^{-1} and a yield of 98%.



Scheme 1 Light-triggered reaction of *o*-nitrobenzyl alcohol with benzylamine in aqueous solution.

Herein reported is the preparation of 1D arrays of gold nanoparticles (Au NPs) in aqueous solutions *via* this light-triggered coupling reaction. We show that the photolysis of light-responsive *o*-nitrobenzyl derivative thioctic acid 3-(3-hydroxymethyl-4-nitrophenoxy)-propyl ester (TNB) functionalized Au NPs (TNB–Au NPs) by UV light triggers the condensation with benzylamine functionalized neighboring Au NPs [thioctic acid 4-aminomethylbenzylamide (TBA) functionalized Au NPs, TBA–Au NPs], that couples these NPs into assemblies by the indazolone linkages (Scheme 2). The topological features of the assemblies were found to be dependent on the irradiation time and the concentration of NPs. With increasing time of irradiation on dilute solution, anisotropic short discrete chains, long branched chains, looped chains and a chain network were progressively produced, which is driven by the anisotropic electrostatic repulsions during the



Scheme 2 Schematic illustration of light-triggered covalent assembling of Au NPs.

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self-assembling of the charged NPs.[7] With solutions containing relatively high concentration of NPs, however, complicated aggregates were found to be dominant. Unlike available fabricating methods for 1D NPs arrays,[2,3,5] the light-triggered assembling strategy does not need any cross-linking ligand or template, thereby representing a spatiotemporally controllable means of covalently assembling NPs in aqueous solutions because of the non-invasive and high spatiotemporal resolution character of light.

To apply the light-triggered coupling reaction in the assembling of Au NPs, Au NPs were functionalized by thiol ligands, TNB and TBA that were obtained from reactions of *o*-nitrobenzyl alcohol and benzylamine respectively with thioctic acid (TA). The light-triggered crosslinking property of these thiol ligands in aqueous solutions was monitored by UV-visible absorption spectra and APCI-MS analysis (Fig. S1 and S2, ESI†). Au NPs with a diameter of 23 nm were obtained by a sodium citrate reduction method.[8] TNB–Au NPs and TBA–Au NPs were prepared by refluxing the citrate-stabilized Au NPs with the corresponding thiol ligands TNB and TBA, respectively. TA was employed as a stabilizing agent together with TNB and TBA to allow the Au NPs to be stably dispersed. The molar ratios of TA to the functionalized thiols loaded on nanoparticles were estimated to be 100 : 1 (for details see ESI†). The Au NPs were further purified by repeated centrifugations and redispersions in H_2O to remove the excess thiols. The as prepared TNB–Au NPs and TBA–Au NPs were well dispersed in aqueous solution and both showed an intense surface plasmon resonance at 520 nm.

The light-triggered assembling of Au NPs was investigated by absorption spectroscopy and transmission electron microscopy (TEM). Assembling of Au NPs in a dilute solution ($A_{520\,nm}$ = 0.074, concentration of Au NPs was indicated by the absorbance at 520 nm) was investigated first. The mixture of the two kinds of functionalized Au NPs in pH 7.4 PBS showed the isotropic surface plasmon band at 520 nm (Fig. 1) and no change was observed after allowing the solution to stand in the dark for 24 h. Irradiation of the solution by UV light (λ > 310 nm) for 5 min induced a slight increase in the absorbance beyond 550 nm. However, a 10-min exposure led to a significant reduction in the absorbance of the 520 nm band as well as the development of a new band at 650 nm that is characteristic of the Au nanochains due to excitation of the plasmon resonance along the long axis of the nanochains.[9]

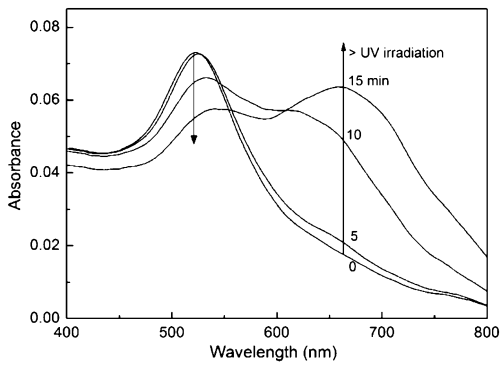


Fig. 1 UV-visible spectra of TNB–Au NPs and TBA–Au NPs in pH 7.4 PBS after irradiation with increasing time.

Further irradiation produced a continuous increase in the absorbance of the low energy band and the spectrum finally shifted to the red to 675 nm, indicating a lengthening of the Au chains.[10] Consistent with the absorption spectral change, the solution turned to blue from the original deep red colour.

TEM images corresponding to the above spectral changes clearly reveal the formation of highly anisotropic 1D Au nanochains. Au NPs were found well dispersed in aqueous solutions as isolated NPs before being exposed to UV light (Fig. 2a). By increasing irradiation time from 5 to 15 min, tri- and tetra-NPs chain-like structures (Fig. 2b), short discrete chains (Fig. 2c) and complex chains of increasing length and branching (Fig. 2d) were developed in the solution in sequence. The Au chains seem to form networks by loop upon a further irradiation (Fig. 2e). It is worth noting from the TEM images that after 30-min irradiation almost all the Au NPs were assembled together with negligible discrete NPs remaining, demonstrating a rapid and highly efficient assembling of the functionalized Au NPs under UV light. Fig. 2f shows a linear chain 200 nm long consisting of 12 NPs. The distance between successive NPs revealed by high resolution transmission electron microscopy (HRTEM) (Fig. 2g) is 1.5 ± 0.4 nm, which is smaller than the size of the formed indazolone linker that is 3.64 nm in length (calculated by gaussian view). This suggests that the observed chain is brought together by the molecular linkers, which are in a molecular folding status.[11]

We next examined the light-triggered assembling of Au NPs in relatively concentrated solution. It was found that, with increasing concentration, the formation of linear superstructures was inhibited and aggregates were instead preferred. In a solution of Au NPs with the absorbance at 520 nm of 0.18, a 30-min UV irradiation led to chain assemblies together with irregular aggregates (Fig. 3a). At a higher concentration of Au NPs ($A_{520\,nm}$ = 0.49), only aggregates were observed after irradiation (Fig. 3b). In control experiments with the solutions containing only the TNB–Au NPs or TBA–Au NPs, no notable spectral change was observed after 45-min irradiation (Fig. S3), indicating that Au NPs do not assemble in these cases. These observations demonstrate that the functionalized

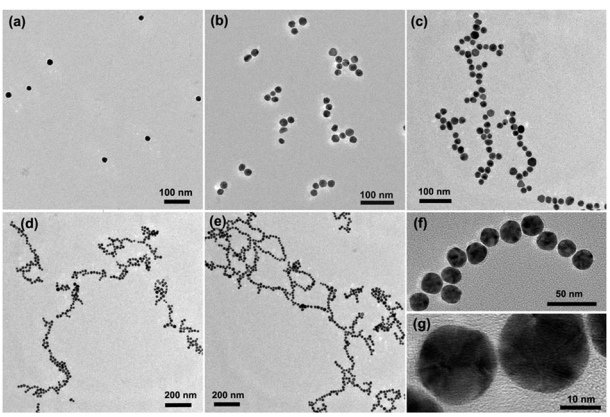


Fig. 2 TEM micrographs of the Au NPs after UV irradiation of increasing time: (a) 0, (b) 5, (c) 10, (d) 15 and (e) 30 min. Images (f) and (g) are the HRTEM characterizations of an obtained Au NPs nanochain.

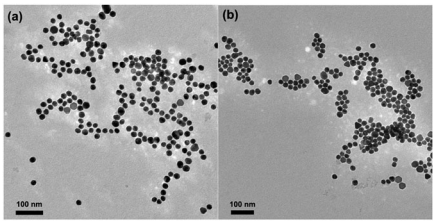
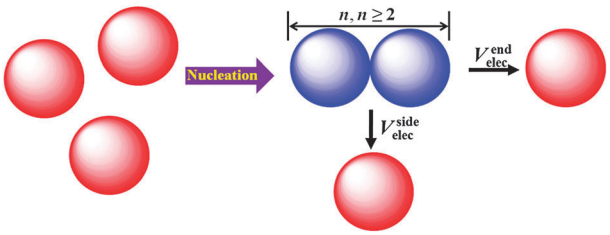


Fig. 3 TEM micrographs of the Au NPs solutions of different concentration after 30-min UV irradiation: $A_{520\,nm}$ = 0.18 (a) and 0.49 (b).



Scheme 3 Electrostatic repulsions between NPs during the assembling.

Au NPs self-assemble only under UV irradiation when a covalent reaction takes place and the superstructure of assemblies can be facilely regulated by varying UV irradiation time and/or the concentration of NPs.

The formation of anisotropic 1D Au NPs arrays can be rationally attributed to the anisotropic electrostatic repulsions during the self-assembling of the charged NPs. The mixture of the two kinds of Au NPs is stable in PBS solution because of the strong electrostatic repulsion among the NPs that were negatively charged from the TA ions. Photolysis of the TNB–Au NPs generates NPs counterparts bearing now *o*-nitrosobenzaldehyde groups that act as reactive sites towards TBA moieties on the TNB–Au NPs surface. Random collision and nucleophilic reaction couple the initial two kinds of NPs into a dimer-like structure (Scheme 3). However, the weaker electrostatic repulsion at the end of a chain in proximity to an NP (V_{elec}^{end}) than that between the chain-side and a neighboring NP (V_{elec}^{side}) allows other NPs to preferentially attach to the ends of the dimer, rather than to the sides.[7a] As a consequence, extended 1D nanoparticle assemblies in the form of trimers, tetramers, short discrete chains, long branched chains, looped chains, and a chain network are formed in sequence as the solution of TNB–Au NPs at a low concentration in the presence of TBA–Au NPs is exposed to the UV light for an increasing time. However, at higher concentration the formation of aggregations may result from the increased probability of collision at the chain sides.

In conclusion, covalent fabrication of 1D arrays of Au NPs in aqueous solution was achieved by using a light-triggered coupling reaction between *o*-nitrobenzyl alcohol and benzylamine moieties respectively functionalized on the surface of NPs. Photolysis of TNB functionalized Au NPs surface under UV light generates reactive sites on the surface of NPs towards TBA–Au NPs. Balanced by electrostatic repulsion, the TNB–Au NPs in dilute solution under UV light tend to couple TBA–Au NPs in the form of chains and networks while aggregates were preferred in the solutions of Au NPs of higher concentration. This strategy represents a spatiotemporally controllable means for covalently assembling Au NPs into 1D architectures in aqueous solutions and can in principle be extended to other applications in material sciences and biochemistry.

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